

# MAP PRECIPITATION FROM LANDFILL LEACHATE AND SEAWATER BITTERN WASTE

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## ABSTRACT

The leachates generated at Hong Kong landfill sites contain high strength of ammonium-nitrogen ( $\text{NH}_4^+\text{-N}$ ) over 3,000  $\text{mg l}^{-1}$  and are generally inhibitive to most biological treatment processes. To remove the  $\text{NH}_4^+\text{-N}$  from the landfill leachates and also recover the nitrogen as a struvite fertilizer, a lab-scale study was performed to investigate the feasibility of  $\text{NH}_4^+\text{-N}$  removal and struvite crystallization using different magnesium sources. Three combinations of chemicals,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgO} + \text{H}_3\text{PO}_4$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$ , were first used at different molar ratios to precipitate  $\text{NH}_4^+\text{-N}$  from the leachate. The experimental results indicated that  $\text{NH}_4^+\text{-N}$  were removed by 92%, 36% and 70% respectively at pH 9.0 and a molar ratio of  $\text{Mg:N:P} = 1:1:1$ . Two synthetic seawater bittern wastes containing  $\text{Mg}^{2+}$  at 9,220  $\text{mg l}^{-1}$  and 24,900  $\text{mg l}^{-1}$  respectively were then used as a magnesium source, while 85%  $\text{H}_3\text{PO}_4$  chemical was used as a phosphorus source. The results revealed that  $\text{NH}_4^+\text{-N}$  was removed by 80% and 72% respectively, while a molar ratio of  $\text{Mg:N:P} = 1:1:1$  was applied. In the final stage of experiments, the magnesium-ammonium-phosphate (MAP) precipitates were examined by SEM, EDS and XRD. The SEM micrographs of the MAP precipitates showed a typical morphology of elongated tubular and short prismatic crystals. The EDS and XRD results indicated that the chemical composition of

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the MAP precipitates depended on the chemicals used and experimental conditions. The study confirmed that the recovery of  $\text{NH}_4^+\text{-N}$  from landfill leachate and seawater bittern wastes could be effectively achieved by MAP precipitation to obtain struvite crystals with a composition of 5.1%N, 10.3%Mg and 16.5%P.

*Key words*—Landfill leachate, ammonium-nitrogen, magnesium ammonium phosphate (MAP), struvite, crystallization and precipitation.

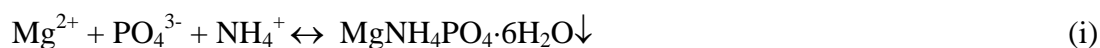
## INTRODUCTION

Biological nitrification is normally employed for ammonia removal from low strength wastewaters, while air stripping is usually applied for ammonia removal from high strength wastewaters.

Landfill leachates in Hong Kong are usually enriched by a high concentration of  $\text{NH}_4^+\text{-N}$  about 3,000 - 6,000  $\text{mg l}^{-1}$  and this has toxic inhibition to microorganisms [1]. Currently, aerobic biological processes are engaged for leachate treatment at the main landfill sites in Hong Kong. To eliminate the microbial inhibition caused by ammonia in the processes, a high ratio (300 - 400%) of effluent recirculation must be applied to eliminate the ammonia strength in the reactors. Although this high effluent recirculation operation can technically solve the problem, it reduces the volumetric loading of the reactors greatly and results in a very high treatment cost of more than HK\$100  $\text{m}^{-3}$ . In addition, a large space is also required for construction of those bioreactors.

Alternatively chemical precipitation can also be applied to remove  $\text{NH}_4^+\text{-N}$  from leachate with specific selectivity, in which additional magnesium ( $\text{Mg}^{2+}$ ) and phosphate ( $\text{PO}_4^{3-}$ ) need to be added to produce an insoluble precipitate of magnesium ammonium phosphate (MAP) with a chemical formula of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . The basic chemical reaction of MAP formation is shown in Equation

i.



magnesium-ammonium-phosphate has a specific gravity of 1.71 and a low solubility of 0.023 g (100 ml)<sup>-1</sup>-H<sub>2</sub>O at 0°C, which is well known as struvite in analytical chemistry and can be used directly as a fertilizer material or as a substitute raw material in standard fertilizer production technology [2]. While only slightly soluble in water and soil solutions, struvite has been found to be a highly effective source of phosphorus, nitrogen and magnesium for plants through both foliar and soil application. When properly granulated, MAP can be applied to soil at rates greatly exceeding those of conventional fertilizers without danger of burning plant roots. In addition, less frequent application of MAP is allowed. Therefore, MAP has been used commercially for container potted plants and also proven to be appropriate for use on turf, tree seedlings, ornamentals, vegetables and flower boards [3].

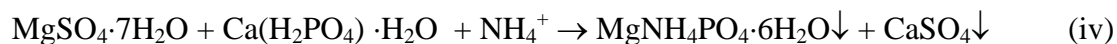
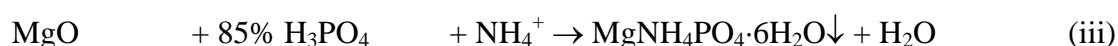
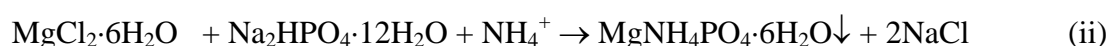
Chemical processes from such raw materials of magnesium oxide, phosphorus acid and ammonia can produce struvite, but this is not commonly done, as the costs are usually prohibitive. To reduce the cost of chemicals, Shin and Lee [4] suggested bittern and seawater, containing Mg<sup>2+</sup> of 31,390 mg l<sup>-1</sup> and 1,136 mg l<sup>-1</sup> respectively, are excellent coagulants for nutrient removal from industrial wastewater. Seawater with 1,250 mg l<sup>-1</sup> Mg<sup>2+</sup> has also been tested by Matsumiya *et al.* [5] to remove phosphorus from digester sludge dewatering liquor by crystallization of MAP. A study of the production of multi -nutrient phosphatic base fertilizers from seawater bittern and phosphoric acid has proven the possibility of production a salt with its composition of Mg 19%, K 6%, PO<sub>4</sub> 67% and B 0.1% [6]. Besides, seawater bittern has also served as coagulants in treating emulsified oil and alkaline wastewaters [7, 8, 9]. Compared to other magnesium sources such as MgCl<sub>2</sub> and MgSO<sub>4</sub>, bittern is a reject by-product from solar seawater evaporation ponds in sea salt production industry. As predicted by Münch and Barr [3], it may become economical to operate the MAP

processes for ammonia removal if the MAP product as struvite can be sold at a favourable price. However, limited works has been conducted on simultaneous removal and recovery of ammonia-nitrogen from nitrogen-rich landfill leachate. This study was aimed at (i) determining the removal efficiency of  $\text{NH}_4^+\text{-N}$  from landfill leachate by adding both chemicals and seawater bittern waste as a rich source of  $\text{Mg}^{2+}$ , and (ii) investigating the physio-chemical properties of the generated MAP precipitates.

## MATERIAL AND METHODS

### Leachate samples and chemicals

Raw leachate samples were collected from the NENT landfill site located in the New Territory of Hong Kong and stored in a cool room at 4°C prior to the experiment. Three combinations of chemicals including  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgO} + 85\% \text{H}_3\text{PO}_4$ , and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$  were supplied with analytical grade from BDH and used without any further purification. The chemical reactions are shown in Equations ii - iv.



The amounts of chemicals required to precipitate  $\text{NH}_4^+\text{-N}$  can be stoichiometrically calculated on a basis of the above chemical reactions.

### Seawater bittern samples

In this study, seawater samples containing approximately 3.5% of dissolved salts and  $1,275 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$  were collected from the local seashore near Victoria Harbour, Hong Kong. To prepare

magnesium-rich bittern waste samples, seawater was gently evaporated to 12% and 4.2% of its original volume at 60°C, respectively. The bittern sample with 12% of its original volume contained 9,000 mg l<sup>-1</sup> of Mg<sup>2+</sup> and the bittern sample with 4.2% of its original volume contained 24.9 g l<sup>-1</sup> of Mg<sup>2+</sup>, which is slightly lower than 31.39 g l<sup>-1</sup> [4] and 31.37 g l<sup>-1</sup> [6] of Mg<sup>2+</sup> in the real bittern wastes from natural salt works.

### **Jar test procedure**

The MAP precipitation tests were carried out in 1-L beakers as a batch mode. The experimental procedures are outlined below: (a) 500 ml leachate samples were placed in the beakers; (b) the weighed magnesium salt was added into the beakers first and the weighed phosphate was then added into the beakers; (c) magnetic stirrers were placed at the bottom of beakers to mix the samples during reaction; (d) each reaction lasted for about 15 min and the pH was monitored to determine an equilibrium state when pH became stable; (e) the magnetic stirrers were then switched off and the suspension were kept in still condition to settle for another 15 min; (f) samples were taken from supernatant for analysis; (g) pH of samples was further adjusted to a desired level by dropping 10M NaOH solution into the beakers while stirring, and the suspension was kept for settling again; (h) the supernatant above the MAP precipitates was taken to measure the required parameters and the settled sludge from the liquid was also taken for determining its characters thereafter.

### **Analyses**

Both pH and NH<sub>4</sub><sup>+</sup>-N concentration were measured using an expandable ion analyser (EA940, Orion Research Corporation). Conductivity was measured using a conductivity meter (ES-14E, Horiba Ltd., Japan). Total P as well as the metals of Fe, Mn, Cd, Cr, Cu, Ni, Pb and Zn were

analysed by inductively coupled plasma (ICP, Optima 3300DV, Perkin Elmer) after sample digestion. Other metals of K, Na, Mg and Ca were determined by Atomic Absorption Spectrometer (AAS 3300, Perkin Elmer). The parameters including total dissolved solids (TDS), fixed dissolved solids (FDS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD<sub>5</sub>) were measured with the standard methods [10]. The morphology and composition of the generated MAP precipitates were also analysed. For this, the precipitates were first filtered through a 0.45 µm filter and then dried in an oven at a temperature below 60°C to minimize water loss during crystallization [11]. The crystal morphology of the MAP precipitate was observed with a scanning electron microscope (SEM, Leica Stereoscan 440). The MAP composition analyses were conducted with Energy Dispersive Spectroscopy (EDS, Oxford Model 5526), with an accelerating voltage of 10.0 kV, and further confirmed with an X-ray Diffractometer (XRD, D8 Advance, Bruker axs) analyses, with step scanning of step size 0.030° and step time 1 s.

## **RESULTS AND DISCUSSION**

### **MAP precipitation using three combinations of chemicals**

The leachate sample collected at the NENT landfill site had typical characteristics of the leachate from an aging or aged methanogenic landfill, which is peaty brown and slightly ammoniacal, and had high conductivity and alkalinity, low ratio of BOD<sub>5</sub>/COD and an elevated NH<sub>4</sub><sup>+</sup>-N concentration as summarized in Table 1.

[Table 1]

To investigate the effectiveness of chemical precipitation to remove NH<sub>4</sub><sup>+</sup>-N from the landfill leachate, raw leachate samples containing NH<sub>4</sub><sup>+</sup>-N concentration of 2,750 mg l<sup>-1</sup> were tested by

adding three combinations of chemicals,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgO} + \text{H}_3\text{PO}_4$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$  at a molar ratio of  $\text{Mg}:\text{N}:\text{P} = 1:1:1$ . The residual  $\text{NH}_4^+ - \text{N}$  concentration in the leachate supernatant after precipitation at different pH levels is illustrated in Figure 1. In these tests, it was found that the initial pH 8.50 dropped immediately, after adding the different chemicals, to 6.75, 6.16 and 5.69 respectively. To minimize the residual  $\text{NH}_4^+ - \text{N}$  in the leachate, the pH was adjusted by adding 10M NaOH solution to a final pH 11. In the mean time, it was found that the MAP precipitate formed rapidly and settled quickly at the bottoms of beakers as soon as stirring was switched off. While pH was increasing from 7 to 9, the residual  $\text{NH}_4^+ - \text{N}$  concentration decreased extensively, and while pH was changing from 9 to 11, the  $\text{NH}_4^+ - \text{N}$  concentration only further decreased slightly. Among the three combinations of chemicals tested, it was found that the addition of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  achieved the most efficient MAP precipitation in the leachate, while the addition of  $\text{MgO} + \text{H}_3\text{PO}_4$  achieved the poorest efficiency as also shown in Figure 1.

[Figure 1]

These phenomenon are similar to our previous work for the treatment of leachate from the WENT landfill site [12]. Since MgO has a limited solubility in water phase, its very slow dissolution in the leachate samples may be the main reason to limit its efficiency in the MAP precipitation. In the precipitation tests, the conductivity of supernatant was also monitored. While the raw leachate had a conductivity of  $26.8 \text{ mS cm}^{-1}$ , the supernatant after precipitation by adding  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgO} + \text{H}_3\text{PO}_4$ , and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$  had conductivity of 49.2, 28.9 and  $31.4 \text{ mS cm}^{-1}$  respectively. These data indicated that the salinity of leachate after precipitation had been increased, especially when  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  were used. Therefore, if precipitation is solely designed for the removal or recovery of  $\text{NH}_4^+ - \text{N}$

from leachate, the addition of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  may be recommended as the best option. However, if precipitation is designed as pretreatment prior to a biological process, the elevated salinity after precipitation needs to be considered as a potential inhibition to bacterial activity. In a condition where both the  $\text{NH}_4^+$ -N removal efficiency and additional salinity generated during the precipitation are taken into account, using the chemicals  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$  may be a complimentary option for MAP precipitation. To minimize the salinity of product liquid in the following MAP precipitation tests, phosphoric acid was applied.

### **MAP precipitation using $\text{H}_3\text{PO}_4$ as a phosphate source and bittern waste as a $\text{Mg}^{2+}$ source**

Undoubtedly, the removal of  $\text{NH}_4^+$ -N by the MAP precipitation consumes a large amount of chemicals including magnesium and phosphate salts. To minimize the magnesium consumption, seawater is possibly an appropriate substitute to the commercial magnesium salts. As well known, bittern is a waste solution of magnesium salts as brine from the preparation of salt from seawater by evaporation, which is the bittern water solution of bromides, magnesium, and calcium salts remaining after sodium chloride is crystallized out of seawater. Therefore, bittern is a common by-product from seawater halite plants and is a rich source of magnesium. When bittern is applied to the MAP crystallization process, it is probable that the simultaneous recovery of nitrogen from leachate and magnesium from bittern will be realized. In this study, MAP precipitation was conducted by adding the prepared bittern samples as the magnesium source and phosphoric acid as the phosphate source. The physico-chemical properties of the prepared two bittern samples were analysed and summarized in Table 2.

[Table 2]



The required amount of bittern for MAP precipitation was determined by stoichiometric calculation. According to Equation (i), at least 1.71 g of  $\text{Mg}^{2+}$  would be consumed to precipitate 1 g of  $\text{NH}_4^+\text{-N}$  from the leachate. Two tests were carried out using phosphoric acid and the bittern samples containing 9.22 g  $\text{l}^{-1}$  and 24.9 g  $\text{l}^{-1}$  of  $\text{Mg}^{2+}$  respectively, while the leachate samples contained an initial  $\text{NH}_4^+\text{-N}$  concentration of 2,700 mg  $\text{l}^{-1}$  with an initial pH 8.38. After adding the bittern sample and phosphoric acid, the pH dropped to 4.5 - 5.0 and then readjusted to 10 - 10.5 by adding 10M NaOH solution. The experimental results are shown in Figure 2. In the test using the bittern containing 9,220 mg  $\text{l}^{-1}$  of  $\text{Mg}^{2+}$ , the residual  $\text{NH}_4^+\text{-N}$  concentration was first reduced from 2,700 mg  $\text{l}^{-1}$  to 1,653 mg  $\text{l}^{-1}$  with a resulting pH 4.60 and further decreased to 508 mg  $\text{l}^{-1}$ , while pH was readjusted to 10.47. In the test using the bittern containing 24,900 mg  $\text{l}^{-1}$  of  $\text{Mg}^{2+}$ , the residual  $\text{NH}_4^+\text{-N}$  concentration was first reduced from 2,700 mg  $\text{l}^{-1}$  to 1,901 mg  $\text{l}^{-1}$  with a resulting pH of 4.96 and further reduced to 603 mg  $\text{l}^{-1}$ , while the pH was readjusted to 7.38. Further increase of pH beyond 7.5 only resulted in a slight  $\text{NH}_4^+\text{-N}$  concentration decrease. These results with high  $\text{NH}_4^+\text{-N}$  residual concentration may indicate that both  $\text{Mg}^{2+}$  and  $\text{H}_3\text{PO}_4^{3-}$  dose ratio could limit further removal of  $\text{NH}_4^+\text{-N}$  from the leachate to form MAP.

[Figure 2]

To determine an optimum ratio of Mg:N:P in the MAP precipitation for the leachate from the NENT landfill, two sets of tests were further carried out by overdosing either Mg or P respectively and the experimental results are shown in Figures 3 and 4.

[Figure 3]

[Figure 4]

Similar to the previous experimental phenomena, there was a sharp pH drop in the bulk solution as soon as the bittern and phosphoric acid were added into the raw leachate at all the dosage levels used. The experimental results shown in Figures 3a and 4a indicated when the Mg:N molar ratio of 1:1 was fixed and P was overdosed to 1:1:1.5, there was no significant further reduction of  $\text{NH}_4^+$ -N compared to the results with the molar ratio of 1:1:1. In another set of tests, when N:P molar ratio of 1:1 was fixed and Mg was overdosed to the ratio of 1.5:1:1, there was slight improvement in  $\text{NH}_4^+$ -N removal (Figures 3b and 4b). These results were similar to the results in a recent study, which indicated that (1) excess ammonium is highly beneficial to MAP precipitation; (2) magnesium ions are a limiting factor on struvite precipitation; and (3) pH 8.5 or greater would be required for effective struvite removal [13]. Based on the above results, it may indicate that an insignificant benefit for  $\text{NH}_4^+$ -N removal could be ascribed to the fact of over-dosing either magnesium ion or phosphate anion. To confirm the results, one more test was conducted to overdose both bittern with  $24,900 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$  and phosphoric acid at a molar ratio of Mg:N:P=1.3:1:1.3. Similar results were achieved as shown in Figure 5, which demonstrated that  $\text{NH}_4^+$ -N concentration was lowered from  $2,860 \text{ mg l}^{-1}$  to  $688 \text{ mg l}^{-1}$  first with a resulting pH 7.1 and was only further reduced slightly by increasing pH from 7.1 to 10.58.

[Figure 5]

To appraise the optimum condition for the  $\text{NH}_4^+$ -N removal and recovery from the leachate with the addition of bittern wastes and phosphoric acid, the experimental results demonstrated that (1) the  $\text{NH}_4^+$ -N concentration in the leachate could be further reduced up to 4 - 5% by overdosing the bittern containing  $9,220 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$  and had no significant enhancement by overdosing phosphoric acid. (2) When bittern containing  $24,900 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$  was used, the residual  $\text{NH}_4^+$ -N in the leachate could be further removed up to 9% by overdosing the bittern waste containing  $24,900 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$ . (3) There was no significant improvement by overdosing 30% of both  $\text{Mg}^{2+}$

and  $\text{PO}_4^{3-}$ . However, the  $\text{NH}_4^+$ -N removal of 70 - 85.9% in this study corresponded well with that obtained by Shin and Lee [4]. In their study, the bittern containing  $31,390 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$  was applied as an excellent coagulant and ammonia was removed from industrial wastewater by 72%. To exploit the mechanism of the relatively lower efficiency with the bittern applied, other affecting factors such as high alkalinity, buffer capacity, salinity and initial  $\text{NH}_4^+$ -N concentration of leachate as well as operational conditions of the jar tests should be further investigated in later work.

### **Characterisation of the MAP precipitates**

In general, MAP is white crystalline powder. However, in our experiment, the MAP precipitates generated from the leachate samples was light-yellow in colour that might be attributed to the peaty brown appearance of the raw leachate. Some physical properties of the MAP precipitates from the leachate of the WENT landfill site was studied in our previous work [12], which concluded the capillary suction time (CST) = 41.4 s, solid content = 27% and dry density =  $2,050 \text{ kg}\cdot\text{m}^{-3}$ . The nature of the MAP sludge indicated that it has a high sludge density with a fast settling velocity similar to sand or grit and a short CST which allows much easier dewatering than bio-sludge or flocculent sludge, if dewatering is required. To further characterize the MAP precipitates in this study, a total of four samples were examined to determine their morphology and chemical composition, including one sample precipitated from the supersaturated solution of  $\text{NH}_4\text{Cl}$ ,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  in deionised water and three samples precipitated out of leachate by adding the bittern containing  $9,220 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$  and  $24,900 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$  and  $\text{H}_3\text{PO}_4$  respectively. The SEM micrographs of two samples are shown in Figure 6.

[Figure 6]

[Table 3]

These SEM results showed that the MAP precipitates were a mixture of elongated thick tubular and short prismatic crystals dominated with a size in the range of 10 - 50  $\mu\text{m}$ . Although these MAP precipitates were dominated with struvite, they typically contained impurities such as calcium phosphate salts [14]. In our test, the bittern sample containing 9,220  $\text{mg l}^{-1}$  of  $\text{Mg}^{2+}$  had a calcium concentration of 650  $\text{mg l}^{-1}$  as shown in Table 2 and the EDS results indicated that the MAP precipitate generated by using this bittern contained 0.54% Ca. Therefore, the crystals as shown in Figure 6a seemed to be more amorphous than the crystals formed by pure chemicals as shown in Figure 6b. Chemical composition of MAP precipitates was analysed by EDS and the results are listed in Table 3. It can be indicated that the purity of struvite was significantly affected by the dose of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  added. When the  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  were less dosed than the stoichiometric ratio indicated by Equation (i), more pure struvite was formed. When the  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  were overdosed, the MAP precipitate contained magnesium and phosphate in excess of 20 – 30% relative to ammonium. These results were also confirmed by the XRD analytical results as shown in Figure 7. For comparison, the XRD pattern (#15-0762) of struvite standard [15] is shown in Figure 7d.

[Figure 7]

The developed crystal habit depended upon the supersaturation of the solution together with the concentration of impurities. As revealed by Abbona and Boistelle in 1979 [16] and reviewed by Durrant *et al.* in 1999 [14], very high levels of supersaturation (i.e. conditions of high growth kinetics, high  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  concentrations and  $\text{pH}>8$ ) promoted the formation of bidimensional and tridimensional twinned crystals. At high supersaturation conditions ( $\text{pH}\sim 7$ ) tubular crystals form, however as supersaturation decreased, crystal habit altered from a tubular formation to an increasing elongation. Regulation of pH played the most important role in preventing side reactions such as magnesium hydroxide ( $\text{p}K_s=11.16$ ) or magnesium hydrogen phosphate ( $\text{p}K_s=5.8$ )

precipitation, both of which formed more quickly than slow crystallizing struvite due to their amorphous nature [17]. These indicated that the precipitate could be a mixture of struvite and the above-mentioned side products.

## CONCLUSIONS

Ammonium-nitrogen presenting at high concentrations in local landfill leachate can be successfully removed by chemical precipitation. When the chemicals of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgO} + 85\% \text{H}_3\text{PO}_4$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$  were added with a molar ratio of  $\text{Mg:N:P} = 1:1:1$ , the  $\text{NH}_4^+$ -N in the leachate was removed by 92%, 36% and 70% respectively. Up to 80% and 72% of  $\text{NH}_4^+$ -N in leachate were also removed by adding phosphoric acid and the bittern wastes containing  $9,220 \text{ mg l}^{-1}$  and  $24,900 \text{ mg l}^{-1}$  of  $\text{Mg}^{2+}$  respectively. The SEM micrographs and the XRD patterns of the MAP precipitates showed typically orthorhombic struvite morphology, being mainly ascribed to the chemicals used and operating conditions. When liquid bittern was applied at a molar ratio of  $\text{Mg:N:P} = 1:1:1$ , the produced MAP precipitate consisted of 5.1%N, 10.3%Mg, and 16.5%P with 72% of  $\text{NH}_4^+$ -N recovery from leachate. The experiment demonstrated that the bittern waste has potential to be an alternative to commercial chemicals for removing and recovering ammonium-nitrogen from landfill leachates.

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Table 1. Characteristics of the leachate from the NENT landfill site

Parameters	Unit	Value
pH		8.50
Conductivity	mS cm <sup>-1</sup>	26.8
TDS	mg l <sup>-1</sup>	8,648
COD	mg l <sup>-1</sup>	3,720
BOD <sub>5</sub>	mg l <sup>-1</sup>	910
NH <sub>4</sub> <sup>+</sup> -N	mg l <sup>-1</sup>	2,750
TP	mg l <sup>-1</sup>	32
ALK (as CaCO <sub>3</sub> )	mg l <sup>-1</sup>	14,520
Mg	mg l <sup>-1</sup>	31.5



Table 2. Characteristics of the prepared bittern wastes and raw seawater samples

Parameters	Seawater (100% V)	Bittern (12% V)	Bittern (4% V)
pH	7.75	7.67	8.19
Density (g ml <sup>-1</sup> at 20°C)	1.028	1.151	1.238
TDS (mg l <sup>-1</sup> )	36,700	152,000	205,000
Conductivity (mS cm <sup>-1</sup> )	48.2	479	778
Na <sup>+</sup> (mg l <sup>-1</sup> )	9,658	78,100	62,100
Mg <sup>2+</sup> (mg l <sup>-1</sup> )	1,010	9,220	24,900
Ca <sup>2+</sup> (mg l <sup>-1</sup> )	950	650	10
K <sup>+</sup> (mg l <sup>-1</sup> )	207	2,980	8,474

**Table 3. Composition of the MAP precipitates and struvite fertilizer**

	N(%)	P(%)	Mg(%)	H <sub>2</sub> O(%)	Source
(0) Pure MAP	5.7	12.6	9.9	44	Münch and Barr (2001) Anonymous (1998)
(1) Precipitate from leachate with bittern (9220 mg l <sup>-1</sup> Mg <sup>2+</sup> ) and H <sub>3</sub> PO <sub>4</sub>	5.1	16.5	6.9	28	This study
(2) Precipitate from leachate with bittern (24900 mg l <sup>-1</sup> Mg <sup>2+</sup> ) and H <sub>3</sub> PO <sub>4</sub>	5.1	16.5	10.3	42	This study
(3) Precipitate from leachate with bittern (24900 mg l <sup>-1</sup> Mg <sup>2+</sup> ) and H <sub>3</sub> PO <sub>4</sub> (Mg:N:P=1.3:1:1.3)	5.4	19.9	11.2	46	This study
(4) Precipitate from deionized water with NH <sub>4</sub> Cl, MgCl <sub>2</sub> ·6H <sub>2</sub> O and H <sub>3</sub> PO <sub>4</sub>	5.5	24.8	14.3	54	This study
(5) MAP from concentrate with Mg(OH) <sub>2</sub>	5.1	12.4	9.1	39	Münch and Barr (2001)
(6) MAP from sidestreams with seawater	5.5	12.5	9.6	42	Matsumiya <i>et al</i> (2000)
(7) MAP from digester effluent with MgCl <sub>2</sub>	5.3	13.3	11.5		Anonymous (1998)
(8) MAP from wastewater with phosphate and magnesium salts	8	41(P <sub>2</sub> O <sub>5</sub> )	25(Mg O)	dehydrated	Anonymous (1998)
(9) Struvite fertilizer	5	27(P <sub>2</sub> O <sub>5</sub> )	15(Mg O)	anhydrous	Anonymous (1998)

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